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(54) PHOTOELECTRIC CONVERSION ELEMENT AND PHOTOELECTRIC CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a coloring matter sensitized photoelectric conversion element and a photoelectric cell that have been improved in a converging efficiencyincident photon-to-current conversion efficiency(IPCE) and short-circuit current density (Jsc).

SOLUTION: This photoelectric conversion element comprises a optical anode with two or more layers composed of porous semiconductor fine particlesa charge transport layer and a counter electrode. The long wavelength edges of the optical-absorption wavelength range of the optical anode of two layers or more (wavelengths on the long-wavelength side where the absorbance of 10% of the absorbance to the maximum absorption wavelength) are different from each other.

CLAIMS

[Claim(s)]

[Claim 1]An optical anode more than two-layer [which consists of a porosity semiconductor particulate].

A charge transfer layer.

A counter electrode.

It is the optoelectric transducer provided with the aboveand long wavelength ends (wavelength by the side of long wavelength which shows 10% of absorbance of an absorbance in maximal absorption wavelength) of

the optical absorption wavelength range of an optical anode more than two-layer [said] differ mutually.

[Claim 2]An optoelectric transducer by which a long wavelength end of an optical absorption wavelength range is arranged more in order of short wavelength in the optoelectric transducer according to claim 1 at the incident light side as for an optical anode more than two-layer [said].

[Claim 3]An optoelectric transducer which laminates 2 or more sets of single cells which consist of an optical anode a charge transfer layer and a counter electrode in the optoelectric transducer according to claim 1 or 2.

[Claim 4]An optoelectric transducer whose relative standard deviation of an open circuit light electromotive voltage which said single cell is electrically combined in parallel and each single cell gives in the optoelectric transducer according to claim 3 is 15% or less.

[Claim 5]An optoelectric transducer whose relative standard deviation of short circuit photoelectric current which said single cell is electrically combined in series and each single cell gives in the optoelectric transducer according to claim 3 is 15% or less.

[Claim 6]An optoelectric transducer to which sensitization of at least one of said the optical anodes is carried out with coloring matter in the optoelectric transducer according to any one of claims 1 to 5.

[Claim 7]An optoelectric transducer to which sensitization of the optical anode nearest to the light incidence side is carried out with coloring matter in the optoelectric transducer according to any one of claims 1 to 6.

[Claim 8]An optoelectric transducer which is coloring matter in which said coloring matter is chosen from coloring matter of an organometallic complex a phthalocyanine system a porphyrin system and a poly methine system in the optoelectric transducer according to claim 6 or 7.

[Claim 9]An optoelectric transducer which a semiconductor particulate which constitutes said each optical anode turns into from at least one sort of a metallic oxide chosen from titanium oxide a zinc oxide a tin oxidation thing a tungsten oxide and a niobium oxidation thing in the optoelectric transducer according to any one of claims 1 to 8.

[Claim 10]An optoelectric transducer which at least two of said optical anodes become from a mutually different metallic oxide in the optoelectric transducer according to any one of claims 1 to 9.

[Claim 11]An optoelectric transducer in which said charge transfer layer is an ion-conductive electrolyte in the optoelectric transducer according to any one of claims 1 to 10.

[Claim 12]An optoelectric transducer in which said charge transfer layer is a room temperature fused salt electrolyte in the optoelectric transducer according to any one of claims 1 to 11.

[Claim 13]A photoelectric cell using the optoelectric transducer according to any one of claims 1 to 12.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the efficient optoelectric transducer by which the semiconductor electrode was laminatedand a photoelectric cell (especially solar cell).

[0002]

[Description of the Prior Art]The foundation established the dye sensitizing of the semiconductor electrode as a means of electrochemical light energy conversion in the 1970s (H. GerischerPhotochem. Photobiol. 16 volumesp243-2601972). Thenit develops into the sensitization method which uses a coloring matter adsorption thin film for an electrode (T. Miyasakaet al. Nature277 volumesp638-6401979**the surface19 volumesp 532 to 541-1981 years)Furthermore particle floc with large adsorption surface area was used for the semiconductorthe extensive improvement of condensing efficiency was achievedand it improved on the level used as a wet solar cell. It is expected that especially the wet solar cell produced by using the porosity condensation layer of the particles of a dye sensitizing titanium oxide semiconductor for an electrode will exceed an amorphous-silicon solar cell in respect of sunlight energy conversion efficiency and low-cost-izing. As the present skill level a ruthenium complex is used for coloring matterthe visible light up to 800-900 nm can be usedand nearly ten sunlight energy conversion efficiency is acquired. Such essential technology is indicated by Nature353 volumesp 737 to 740-1991 years and a U.S. Pat. No. 4927721 itemsaid 5350644 No. JP5-504023Aetc. Condensing of incident lightthe improvement (or improvement in the short circuit photoelectric current density J_{sc}) in the quantum efficiency (IPCE) for entering light reflecting the efficiency of quantum conversion of a photon-electronand improvement in an open circuit light electromotive voltage (V_{oc}) are important in order to improve further the sunlight engineering efficiency of these wet solar cells from now on.

[0003]For this purposeuse for single sensitizing dye Ru complex system

black coloring matter which extended the absorption wavelength field to 920 nm in Chem. Commun. and 1705 to p1706-1997 as improvement by the side of a pigment material and the rate for Mitsutoshi is expanded in a single cell. The art to which Jsc is made to increase is shown.

However, this art of the improvement of final efficiency is insufficient as a result of IPCE. Voc etc. losing in weight on another side which a sensitization wavelength area expands. Although the method of earning efficiency for light utilization combining a dye sensitizing n-type semiconductor is indicated by J. Phys. Chem. B, the 103rd volume, the method of carrying out sensitization of the p-type semiconductor particles to p8940-8943 with coloring matter and using for an optical cathode and WO 99/No. 163599 in this optical cathode. In the cell with which the dye sensitizing efficiency and photoelectric current by the side of an optical cathode combined these in series since it was very low compared with them of an optical anode, the optical cathode side serves as a bottleneck of current and conversion efficiency is not improved.

[0004] On the other hand, although the effect which raises Voc is shown in for example J. Phys. Chem. B, 103 volumes and 9238 to p9332-1999 using the high strontium titanate of a conducting-zone energy level as a near improvement of a semiconductor material, as a result of electron injection's un-increasing the efficiency, IPCE and Jsc decrease, the efficiency of condensing falls and it has not resulted in final improve efficiency.

[0005] Thus, in energy conversion with a dye sensitizing semiconductor, Voc reflecting the energy acquisition reflecting the quantum efficiency of photoelectric conversion of the charge separation of the photoelectric current density Jsc and an electronic-electron hole becomes a relation of a tie in mutually and these simultaneous improvement is difficult.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to provide the optoelectric transducer and photoelectric cell by which the energy conversion efficiency has been improved and is providing the dye sensitizing type optoelectric transducer and photoelectric cell by which condensing efficiency, the child efficiency (IPCE) for incident light quantity and short circuit current density (Jsc) have been improved especially.

[0007]

[Means for Solving the Problem] In view of the above-mentioned purpose, as a result of research, wholeheartedly this invention person, In an optoelectric transducer which has an optical anode more than two-layer [which consists of a porosity semiconductor particulate] a charge

transfer layer and a counter electrode. By using two or more optical anodes in which long wavelength ends (wavelength by the side of long wavelength which shows 10% of absorbance of an absorbance in maximal absorption wavelength) of an optical absorption wavelength range differ mutually. It found out that a dye sensitizing type optoelectric transducer by which condensing efficiency and efficiency (IPCE) for incident light quantity and short circuit current density (J_{sc}) have been improved was obtained and thought out to this invention.

[0008] That is, since an optoelectric transducer of this invention condensed incident light efficiently, it laminated two or more optical anodes in which optical absorption wavelength ranges differ.

[0009] An optoelectric transducer of this invention is used for a photoelectric cell of this invention.

[0010] When this invention fulfills a following condition, an optoelectric transducer which has the further outstanding photoelectric conversion efficiency is obtained.

[0011] (1) As for an optical anode more than two-layer [said] it is preferred that a long wavelength end of an optical absorption wavelength range is arranged more in order of short wavelength at the incident light side.

[0012] (2) Laminating 2 or more sets of single cells which consist of an optical anode, a charge transfer layer and a counter electrode has preferred things. It is preferred that relative standard deviation of an open circuit light electromotive voltage which said single cell is electrically combined in parallel and each single cell gives is 15% or less, or relative standard deviation of short circuit photoelectric current which said single cell is electrically combined in series and each single cell gives is 15% or less.

[0013] (3) It is preferred that at least one of said the optical anodes consists of a porosity semiconductor particulate by which sensitization was carried out with coloring matter and it is preferred that an optical anode nearest to the light incidence side consists of a porosity semiconductor particulate by which sensitization was carried out with coloring matter. It is preferred that said coloring matter is coloring matter chosen from coloring matter of an organometallic complex, a phthalocyanine system, a porphyrin system and a poly methine system.

[0014] (4) It is preferred that a semiconductor particulate which constitutes said each optical anode consists of at least one sort of a metallic oxide chosen from titanium oxide, a zinc oxide, a tin oxidation thing, a tungsten oxide and a niobium oxidation thing. It is preferred that at least two of said optical anodes consist of a mutually different

metallic oxide.

[0015] (5) It is preferred that said charge transfer layer is an ion-conductive electrolyte or a room temperature fused salt electrolyte.

[0016]

[Embodiment of the Invention] Since the optoelectric transducer of this invention condenses incident light efficiently two or more optical anodes (photosensitive layer) in which the long wavelength ends of the sensitization wavelength range differ are used. Here the long wavelength end of the sensitization wavelength range means the wavelength by the side of the long wavelength which shows 10% of absorbance of the absorbance in the maximal absorption wavelength of an optical anode. The optical anode in which long wavelength ends differ is producible by choosing the kind and/or sensitizing dye of a semiconductor which are used for a photosensitive layer.

[0017] The optoelectric transducer of this invention laminates a single cell as preferably shown in drawing 1. A single cell is laminated in order of the transparent conductive layer 10a (or conductive layer 10) the under coat 60 the photosensitive layer 20 the charge transfer layer 30 and the transparent counter electrode conductive layer 40a (or counter electrode conductive layer 40). Said photosensitive layer 20 consists of the charge transporting materials 23 which permeated the opening between the semiconductor particulate 21 by which sensitization was carried out with the coloring matter 22 and the semiconductor particulate 21 concerned. One layer or multilayered constitution may be sufficient as a photosensitive layer. The charge transporting material 23 consists of the same ingredient as the material used for the charge transfer layer 30. In order to give intensity to an optoelectric transducer the transparent substrate 50a (or substrate 50) may be formed in the conductive layer 10 and/or counter electrode conductive layer 40 side. In this invention the layer which consists of the conductive layer 10 and the substrate 50 which it is arbitrary and is formed of a "conductive substrate" the counter electrode conductive layer 40 and the substrate 50 it is arbitrary and is formed is called a "counter electrode" below. The thing it was made to make this optoelectric transducer work by connecting with an external circuit is a photoelectric cell.

[0018] In this invention in order to make light reach several photosensitive layers of all from which a sensitization wavelength area differs the photosensitive layer and conductive layer (and the base material used if needed) by the side of light incidence must be optically transparent substantially. The situation of other

photosensitive layers a conductive layer and a base material being transparent similarly and the light which penetrated the upper photosensitive layer penetrating a conductive layer and resulting in a lower layer photosensitive layer must be satisfied. However the conductive substrate of the photosensitive layer of the bottom of the heap may be opaque when the photosensitive layer does not arrange in the lower layer. Similarly when the bottom of the heap is a counter electrode a counter electrode and its base material may be opaque.

[0019] In the single cell shown in drawing 1 coloring matter 22 grade is excited the electron of the high energy in the excited coloring matter 22 grade is passed to the conducting zone of the semiconductor particulate 21 and the light which entered into the photosensitive layer 20 containing the semiconductor particulate 21 by which sensitization was carried out with the coloring matter 22 reaches the conductive layer 10 by diffusion further. At this time the molecule of the coloring matter 22 grade serves as an oxidant. In a photoelectric cell while the electron in the conductive layer 10 works in an external circuit it returns to the oxidant of coloring matter 22 grade through the counter electrode conductive layer 40 and the charge transfer layer 30 and the coloring matter 22 is reproduced. The photosensitive layer 20 works as an optical anode. On the boundaries (for example the boundary of the conductive layer 10 and the photosensitive layer 20 the boundary of the photosensitive layer 20 and the charge transfer layer 30 the boundary of the charge transfer layer 30 and the counter electrode conductive layer 40 etc.) of each layer the constituents of each class may be carrying out diffusive mixing mutually.

[0020] (A) Explain the laminated structure of the element of example this invention of the internal structure of an optoelectric transducer. Two or more optical anodes charge transfer layers and counter electrodes which provide a photosensitive layer are laminated and the element of this invention is constituted. Several optical anodes in which the long wavelength ends of an optical absorption wavelength differ mutually are laminated and constituted still more preferably. That is the element of this invention is made for the purpose of condensing incident light efficiently by lamination of two or more optical anodes.

[0021] Here the example of laminated constitution is shown in drawing 6 from drawing 2. The photosensitive layer 20a which differs in a sensitization wavelength area via the transparent conductive layer 10a to both sides of the water-white base material [like glass] 50a whose drawing 2 is and the photosensitive layer 20b are covered The water-white base material 50a which the charge transfer layer 30 was placed by the

upper layer and lower layer and supported the transparent conductive layer 40a as a counter electrode in the topmost part. The base material 50 which supported the counter electrode conductive layer 40 of light reflex nature opaque as a counter electrode same with the bottom of the heap is arranged and these electrode layers are the cells of the structure laminated by taking electrical junction mutually. 10a and 40a of a conductive layer may be the same substance or may differ from each other. In this cell after light enters from the transparent counter electrode layer side and penetrates the charge transfer layer 30 it passes the photosensitive layer 20a and the photosensitive layer 20b one by one and is reflected by the counter electrode 40 of the bottom of the heap. Here a photosensitive layer is a porous semiconductor layer as for the photosensitive layer 20b it is preferred that the sensitization wavelength area is a long wavelength side more to the photosensitive layer 20a and the light which was not absorbed by the photosensitive layer 20a is absorbed by the lower layer photosensitive layer 20b. As for the charge transfer layer 30 it is preferred that it is a common substance through the whole cell and typically ion-conductive fused salt is used.

[0022] Although drawing 3 is a cell containing the same photosensitive layers 20a and 20b as drawing 2 the order of lamination differs about the photosensitive layer 20a. The top layers are not a counter electrode but the photosensitive layer 20a and its base material the charge transfer layer 30 is placed by the lower layer and the transparent substrate 50a with which the counter electrode 40a of a transparent conductive layer and other one side covered the transparent conductive layer 10a and the photosensitive layer 20b in one side is put on the bottom of it. Under from it is the same as that of drawing 2 and the light which entered is eventually reflected by the reflexivity counter electrode of the bottom of the heap. The composition of drawing 3 is a point of the optical absorption efficiency of the whole photosensitive layer and is more preferred than the composition of drawing 2. That is in drawing 2 since incident light may be first absorbed in part by the charge transfer layer it may be accompanied by the loss of condensing.

[0023] The composition of drawing 4 is an example for which the photosensitive layer from which three sorts of sensitization wavelength areas differ is used. An order of lamination is fundamentally the same as drawing 3 and the photosensitive layer 20c is added to the lower layer of the photosensitive layer 20b on both sides of a counter electrode (40a and 50a). Here as for the sensitization wavelength area of the photosensitive layer 20c being located in the long wavelength side is

more preferred in respect of condensing efficiency than in respect of the sensitization wavelength area of the photosensitive layer 20b. concrete -- the photosensitive layer 20a -- blue - a green field -- the photosensitive layer 20b -- green - the photosensitive layer 20c is designed in a red field have photosensitivity in a red - infrared field. [0024]Drawing 5 is the composition in which the metal lead 11 for reducing the surface resistance of an electrode to the laminated constitution of drawing 4 and raising electrical conduction to it was made to insert. A lead layer usually consists of the narrow shape of a lattice or parallel linear circuit pattern of width. Specifically 1 mm and thickness are provided for line width as 0.1 to 1 micrometer of wiring from 10 micrometers. The metal lead 11 is formed in order to raise the electrical conduction of the transparent conductive layer 10a or the transparent counter electrode 40 and it takes the composition electrically combined with the transparent conductive layer 10a or the transparent counter electrode 40. Specifically a metal lead is inserted between the inside of a transparent conductive layer or the transparent conductive layer 10a and the base material 50a and/or between the transparent counter electrode conductive layer 40a and the base material 50a. This lead layer may be opaque and is typically made with the metallic material of low electric resistance.

[0025]Drawing 6 is an example of the composition using the photosensitive layer which differs in three sorts of sensitization wavelength areas and the common counter electrode of one layer. Use the three transparent base materials 50a like glass and the photosensitive layer 20a is formed in the undersurface of the 1st base material 50a. While forming the photosensitive layer 20b in the upper surface of the 2nd base material 50a, the photosensitive layer 20c is formed in the undersurface. The common counter electrode 40 is formed in the upper surface of the 3rd base material 50a and it consists of composition filled up with the charge transfer layer 30 respectively among said photosensitive layers 20a and 20b and between the photosensitive layer 20c and the counter electrode 40. The photosensitive layers 20a, 20b and 20c and the counter electrode 40 have touched via the charge transfer layer 30 respectively by the leak hole 1a for charge transfer which penetrates the photosensitive layer 20b, the 2nd base material 50a and the photosensitive layer 20c.

[0026] In the basic constitution of drawing 6, various kinds of auxiliary layers can be inserted and used for an improvement of cell performance from drawing 2. Between a photosensitive layer and a transparent conductive layer, an under coat can be provided as a ground of a

photosensitive layer. Lamination is also changeable suitably such as providing the spacer layer for the prevention from an electric short circuit between a photosensitive layer and a counter electrode layer furthermore.

[0027] In the lamination type structure cell of above-mentioned this invention although all methods are possible for the way of each photosensitive layer and electric connection of a counter electrode according to the output (an electromotive voltage and current) made into the purpose a desirable method is a connection method shown below.

1) All the counter electrode is combined in an external circuit and consider it as a common counter electrode and similarly combine the transparent conductive layer of the ground of each photosensitive layer in an external circuit and consider it as a common anode. Namely the laminated-structure type cell which the single cell which consists of combination of a photosensitive layer and a counter electrode is wired in parallel as an equivalent circuit and is constituted.

2) The laminated-structure type cell constituted by each single cell which serves as a counter electrode from the transparent conductive layer of the ground of this and the photosensitive layer which counters connecting in series as an equivalent circuit.

[0028] The equivalent circuit showed to drawing 7 and drawing 8 by making into an example the laminated-structure type cell which consists these of three single cells. The composition (drawing 7) of 1 which consists of parallel circuits is more preferred among above 1 and the composition of two. The combination circuit which adopted both of wiring forms (as in-series as parallel) of 1 and 2 can also be used for the cell of this invention.

[0029] The output characteristics of the single cell which constitutes a lamination type cell in relation to the above-mentioned wiring form are the purposes of securing the stability of the performance of a lamination type cell and it is preferred to fulfill one of the following conditions.

** The percentage which the standard deviation of the open circuit electromotive voltage (V_{oc}) which two or more single cells which consist of an optical anode and a counter electrode are electrically combined in parallel in the equivalent circuit of the cell which laminated these single cells and each single cell gives gives to average value should be less than 15%.

** The percentage which the standard deviation of the short circuit photoelectric current (I_{sc}) which two or more single cells which consist of an optical anode and a counter electrode are electrically combined in

series in the equivalent circuit of the cell which laminated these single cells and each single cell gives to average value should be less than 15%.

[0030] (B) It is necessary to use a transparent conductive material from the necessity for light transmission except the conductive substrate of the conductive substrate bottom of the heap. A transparent conductive base material is constituted by a transparent conductive layer and two-layer [of the transparent substrate which supports it]. As a conducting agent used for a transparent conductive layer metal carbon (for example platinum gold silver copper aluminum rhodium indium etc.) or conductive metallic oxide (what doped fluoride to an indium tin multiple oxide and the tin oxide) is mentioned. A thing desirable from an optical transparency point in this is conductive metallic oxide (diacid-ized tin which doped especially fluoride).

[0031] A conductive substrate is so good that surface resistance is low. The range of desirable surface resistance is below 100 ohms / ** and is below 40 ohms / ** still more preferably. Although there is no restriction in particular in the minimum of surface resistance they are usually 0.1 ohm / ** grade.

[0032] A transparent conductive base material needs a substantially transparent thing in the wavelength range of 400-900 nm as for the transmissivity of the whole light it is preferred that it is not less than 50% and it is preferred that it is especially not less than 70%.

[0033] As for the coverage of conductive metallic oxide in order to secure sufficient transparency and to give high conductivity it is preferred to consider it as per [0.01-100 g] base material 1m^2 . As for the thickness of the conductive layer about 0.02-10 micrometers is preferred.

[0034] What formed the transparent conductive layer which consists of conductive metallic oxide in the surface of transparent substrate such as glass or a plastic by spreading or vacuum evaporation as a transparent conductive base material is preferred. The electrically conductive glass which deposited the conductive layer which consists of diacid-ized tin which doped fluoride especially on the transparent substrate made with the soda lime float glass of low cost is preferred. In order to consider it as a flexible optoelectric transducer or solar cell by low cost it is good to use for a transparent polymer film what provided the conductive layer. As a material of a transparent polymer film a tetraacetyl cellulose (TAC) Polyethylene terephthalate (PET) polyethylenenaphthalate (PEN) Syndiotactic poly styrene (SPS) a polyphenylene sulfide (PPS) There are polycarbonate (PC) polyarylate (PAR) polysulfone (PSF) polyester sulfone (PES) polyether imide (PEI) cyclic polyolefin bromine-ized

phenoxy etc. As for the coverage of conductive metallic oxide in order to secure sufficient transparency it is preferred to consider it as per [0.01-100g] base material 1m² of glass or a plastic.

[0035] It is preferred to use a metal lead in order to lower resistance of a transparent conductive base material. The construction material of a metal lead has preferred metals such as aluminum, copper, silver, gold, platinum and nickel and is preferred. [of especially aluminum and silver] As for a metal lead it is preferred to install in a transparent substrate by vacuum evaporation, sputtering etc. and to provide on it the tin oxide which doped fluoride or the transparent conductive layer which consists of ITO films. After providing a transparent conductive layer in a transparent substrate it is also preferred to install a metal lead on a transparent conductive layer. The fall of the incident light quantity by metal lead installation may be 1 to 5% more preferably less than 10%.

[0036] (C) In a photosensitive layer photosensitive layer a semiconductor acts as what is called a photo conductor absorbs light performs charge separation and produces an electron and an electron hole. In the semiconductor particulate by which dye sensitizing was carried out generating of optical absorption the electron by this and an electron hole takes place mainly in coloring matter and a semiconductor particulate receives this electron and bears the role to transmit. As for the semiconductor used by this invention it is preferred that it is an n-type semiconductor which gives anode current by a conductor electron serving as a carrier under optical pumping.

[0037] (1) An element semiconductor like silicon and germanium as a semiconductor particulate semiconductor particulate the chalcogenide (for example an oxide and a sulfide.) of an III-V system compound semiconductor and metal Compounds (for example strontium titanate, titanate, niobate, etc.) etc. which have a perovskite structure such as a selenide can be used.

[0038] As desirable metal being chalcogenide, titanium, tin, zinc, iron, tungsten, zirconium, hafnium, strontium, indium, cerium, The oxide of yttrium, a lantern, vanadium, niobium, tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of bismuth, cadmium or a leaden selenide, the telluride of cadmium etc. are mentioned. As other compound semiconductor, the selenide of phosphide, such as zinc, gallium, indium and cadmium, gallium arsenide or copper-indium, the sulfide of copper-indium etc. are mentioned.

[0039] The desirable example of the semiconductor used for this invention Si, TiO₂, SnO₂, Fe₂O₃, WO₃, ZnO, Nb₂O₅, CdS, ZnS, PbS, Bi₂S₃, CdSe, CdTe, GaP, InP, GaAs, CuInS₂, Are CuInSe₂ etc. and more preferably TiO₂, ZnO, SnO₂, Fe₂O₃, WO₃ It is

Nb_2O_5 , CdS , PbS , CdSe , InP , GaAs , CuInS_2 or CuInSe_2 is TiO_2 or Nb_2O_5 especially preferably and is TiO_2 most preferably.

[0040] A single crystal or polycrystal may be sufficient as the semiconductor used for this invention. Although the single crystal from a viewpoint of conversion efficiency is preferred from viewpoints of a manufacturing cost, raw-material reservation and an energy payback time etc., polycrystal is preferred and especially the porous membrane that consists of semiconductor particulates is preferred.

[0041] Although the particle diameter of a semiconductor particulate is generally an order of nm- μm as for the mean particle diameter of the primary particle for which it is asked from the diameter when the projected area was converted into the circle, it is preferred that it is 5–200 nm and its 8–100 nm is more preferred. As for the mean particle diameter of the semiconductor particulate (aggregated particle) in dispersion liquid, 0.01–10 micrometers is preferred.

[0042] Two or more kinds of particles from which particle size distribution differs may be mixed and it is preferred that the average size of small particles is 5 nm or less in this case. Particle diameter is big for example, about 300-nm semiconductor particle may be mixed in order to scatter incident light and to raise an optical capturing rate.

[0043] As a method of producing a semiconductor particulate, Sumio Sakuhana's company of the "science of sol-gel method" AGUNE ** style (1998) A sol-gel method given in "the thin-layer-coating art by a sol-gel method" (1995) etc. of TECHNICAL INFORMATION INSTITUTE composition of the monodisperse particle by the new synthetic method gel -**** method and size gestalt control of Tadao Sugimoto -- wait -- **** the 35th volume No. 9 and the gel -**** method of a 1012–1018 pages (1996) statement are preferred. The method of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an acid water matter salt is also preferred.

[0044] When a semiconductor particulate is titanium oxide, each of above-mentioned sol-gel method, gel -**** methods and elevated-temperature hydrolysis methods in the inside of the acid water matter salt of a chloride is preferred but the sulfuric acid method and chlorine method of a statement can also be further used for Manabu Seino's "titanium oxide physical-properties and applied-technology" Gihodo Shuppan (1997). Furthermore, as a sol-gel method, the method of the journal OBU American ceramic society of varvesthe 80th volume No. 12 and a 3157–3171 pages (1997) statement The method of chemistry OBU MATERIARUZU of burn sidethe 10th volume No. 9 and a 2419–2425-page statement is also preferred.

[0045] (2) In order to apply the formation semiconductor particulate of a

semiconductor particle layer on a conductive substrate the above-mentioned sol-gel method other than the method of applying the dispersion liquid or the colloidal solution of a semiconductor particulate on a conductive substrate etc. can also be used. When fertilization of an optoelectric transducer the physical properties of semiconductor particulate liquid the flexibility of a conductive substrate etc. are taken into consideration the wet film production method is comparatively advantageous. As the wet film production method the applying method and print processes are typical.

[0046] When compounding the method and semiconductor which are distributed while grinding as a method of producing the dispersion liquid of a semiconductor particulate using the method and mill which are mashed with a mortar other than the above-mentioned sol-gel method the method of depositing as particles and using it as it is in a solvent etc. are mentioned.

[0047] As carrier fluid it is usable in water or various kinds of organic solvents (for example methanol ethanol isopropyl alcohol dichloromethane acetone acetonitrile ethyl acetate etc.). In the case of distribution polymer a surface-active agent a chelating agent etc. may be used as a distributed auxiliary agent if needed.

[0048] As a coating method the air knife method the braid method etc. the roller method a dip method etc. as a meter ring system as an application system as that where application and a meter ring are made at identical parts The slide hopper method given in the wire bar method currently indicated by JP58-4589Ba U.S. Pat. No. 2681294 itemsaid 2761419 No. the 2761791 No. etc. the extrusion method the curtain method etc. are preferred. Spin method and a spray method are also preferred as a general aviation. As a wet printing method letterpress offset and the three major print processes of photogravure are begun and an intaglio a rubber plate screen-stencil etc. are preferred. According to liquid viscosity or wet thickness the desirable film production method is chosen from these.

[0049] The viscosity of the dispersion liquid of a semiconductor particulate is greatly influenced with additive agentssuch as a kind of semiconductor particulate dispersibility and a use solvent kind a surface-active agent and a binder. In a viscous liquid (for example 0.01 - 500 Poise) the extrusion method the cast method screen printing etc. are preferred. It is able for the slide hopper method the wire bar method or spin method to be preferred and to make it a uniform film with hypoviscosity liquid (for example 0.1 or less Poise). If there is a certain amount of coverage spreading according to the extrusion method also by the case of hypoviscosity liquid is possible. Thus what is

necessary is just to choose the wet film production method suitably according to the viscosity of coating liquid, coverage, base material, spreading speed, etc.

[0050] The layer of a semiconductor particulate can carry out multilayer spreading of the dispersion liquid of a semiconductor particulate with which not only a monolayer but particle diameter is different or can also carry out multilayer spreading of the coating layer containing the semiconductor particulate (or a different binder/additive agent) from which a kind differs. Also when thickness is insufficient, multilayer spreading is effective at one-time spreading. The extrusion method or the slide hopper method is suitable for multilayer spreading. When carrying out multilayer spreading, a multilayer may be applied simultaneously and two coats may be given one by one about ten times from several times. When giving two coats further one by one, screen printing can also be used preferably.

[0051] Since the support pigment quantity per unit project area increases so that the thickness (it is the same as the thickness of a photosensitive layer) of a semiconductor particle layer generally becomes thick, the capturing rate of light becomes high but since the generated diffusion length of electron increases, the loss by electric charge recombination also becomes large. Therefore, the desirable thickness of the semiconductor particle layer of each optical anode is 0.5–30 micrometers. Since layers other than the bottom of the heap of the opposite hand of light incidence need to make light penetrate while performing optical absorption, as for the thickness of a semiconductor particle layer, 1–10 micrometers is preferred, 2–9 micrometers are more preferred, and its 4–7 micrometers are still more preferred. The bottom of the heap may be thicker than this. In each optical anode, per base material 1m^2 of a semiconductor particulate, as for coverage, 0.5–30g are preferred, and 3–12g are more preferred.

[0052] Heat-treating is preferred in order to raise improvement in film strength and adhesion with a base material while contacting semiconductor particulates electronically after applying a semiconductor particulate on a conductive substrate. The range of desirable cooking temperature is not less than 40 °C and less than 700 °C and is not less than 100 °C and 600 °C or less, more preferably. Cooking time is 10 minutes – about 10 hours. When using the low base material of the melting point or softening temperature like a polymer film, high temperature processing is not preferred in order to cause degradation of a base material. It is preferred that it is low temperature as much as possible also from the viewpoint of cost. Low temperature-ization becomes possible by

concomitant use of the small semiconductor particulate of 5 nm or less described previously heat-treatment under existence of mineral acid etc. [0053] It is the purpose of increasing the surface area of conductor particles in the second half of heat-treatment or raising the purity near the semiconductor particulate and raising the electron injection efficiency from coloring matter to semiconductor particles and electrochemical plating treatment using chemical plating and titanium trichloride solution using a titanium tetrachloride aqueous solution may be performed for example.

[0054] As for a semiconductor particulate what has large surface area is preferred so that much coloring matter can be adsorbed. For this reason as for the surface area in the state where the layer of the semiconductor particulate was applied on the base material it is preferred that they are 10 or more times to a project area and it is preferred that they are further 100 or more times. Although this maximum does not have restriction in particular they are usually about 1000 times.

[0055] (3) As sensitizing dye used for a coloring matter photosensitive layer organometallic complex coloring matter methine coloring matter porphyrin system coloring matter and phthalocyanine system coloring matter are preferred. Since the wavelength band of photoelectric conversion is made large as much as possible and conversion efficiency is raised two or more kinds of coloring matter is mixable. The coloring matter to mix and its rate can be chosen so that it may double with the target wavelength band and intensity distribution of a light source.

[0056] As for such coloring matter it is preferred to have the suitable bond groups (interlocking group) to the surface of a semiconductor particulate. As desirable bond groups a COOH group an OH radical an SO_3H basis The chelation group which has pi conductivity like a cyano group a $\text{P}(\text{O})(\text{OH})_2$ group a $-\text{OP}(\text{O})(\text{OH})_2$ group or oxime diimine hydroxyquinoline salicylate and an alpha-keto enone rate is mentioned. A COOH group a $\text{P}(\text{O})(\text{OH})_2$ group and especially a $-\text{OP}(\text{O})(\text{OH})_2$ group are especially preferred. These bases may form the alkaline metal etc. and the salt and may form inner salt. If an acidic group is contained like [in case a methine chain forms a squarylium ring and a crocodile NIUMU ring] in the case of poly methine coloring matter it will be good also considering this portion as bond groups.

[0057] Hereafter the desirable coloring matter used for a photosensitive layer is explained concretely.

[0058] (a) As for a metal atom when metal-complex-coloring-matter coloring matter is metal complex coloring matter it is preferred that it is ruthenium Ru. As ruthenium complex coloring matter for example A U.S. Pat.

No. 4927721 itemsaid 4684537 No. The complex pigment of a statement is mentioned to No. world JP98B / [said 5084365 No. said 5350644 No. said 5463057 No. said 5525440 No. JP7-249790A Patent Publication Heisei No. 504512 / ten to /and] 50393 etc.

[0059]The ruthenium complex coloring matter furthermore used by this invention is following general formula (I): $(A_1)_p Ru (B-a) (B-b) (B-c) \dots$ (I)

It is preferred for it to be alike and to be expressed more. A_1 expresses the ligand chosen from the group which consists of $ClSCNH_2$, $OBrICNNO$ and $SeCN$ among general formula (I) and p is an integer of 0-3. $B-a$, $B-b$ and $B-c$ are the following formulas B-1 to B-10 independently respectively. : [0060]
[Formula 1]

[0061] (However if R_{11} expresses a hydrogen atom or a substituent and considers it as a substituent.) The alkyl group which is not replaced [substitution with a halogen atom and 1-12 carbon atoms or] The aryl group which is not replaced [substitution with the aralkyl group which is not replaced / substitution with 7-12 carbon atoms or / or 6-12 carbon atoms or] A carboxylic acid group and a phosphate group (the acid radical of these may form the salt) are mentioned Straight chain shape or branched state may be sufficient as the alkyl part of an alkyl group and an aralkyl group and a monocycle or polycyclic (a condensed ring a ring set) may be sufficient as the aryl portions of an aryl group and an aralkyl group. The organic ligand chosen from the compound expressed is expressed. $B-a$, $B-b$ and $B-c$ may be the same or may differ from each other.
[0062] Although a desirable example of metal complex coloring matter is shown below this invention is not limited to these.

[0063]

[Formula 2]

[0064]

[Formula 3]

[0065]

[Formula 4]

[0066] (b) The methine coloring matter with preferred coloring matter used for methine coloring matter this invention is poly methine coloring mattersuch as cyanine dyemerocyanine dyeand SUKUWARIRIUMU coloring matter. In thesemerocyanine dye and squarylium coloring matter are preferred.

[0067] About a synthetic method of these coloring matter. F. M. Harmer (F. M. Hamer) work "heterocyclic party *****- Cyanine Dyes and Related Compounds (Heterocyclic Compounds-Cyanine Dyes.) and Related Compounds" John Willie and Sons (John Wiley & Sons)-New York London 1964 annual publications Day em Sturmer (D. M. Sturmer) work "heterocyclic Compounds-Special topics in heterocyclic chemistry (Heterocyclic Compounds-Special.) topics in heterocyclic chemistry" Chapter 18 Section 14 the 482nd to 515 pages John - Willie and Sons (John Wiley & Sons)-New York London 1977 annual publications ROZZU chemistry OBU carbon party UNZU (Rodd's Chemistry of Carbon Compounds) 2nd. Ed. vol. IV part B 1977 **Chapter 15 the 369th to 422 pages ERUSEBIA science public company ink (Elsevier Science Publishing Company Inc.) company **New York the British patent No. 1077611 Ukrainskii Khimicheskii Zhurnal the 40th volume It is indicated in literature etc. which were quoted by No. 3253-258 pages Dyes and Pigments the 21st volume 227-234 pages and these articles.

[0068] In addition phthalocyanine and naphthalocyanine and the derivativemetal phthalocyanines Metal naphthalocyanine the porphyrins containing the derivativetetraphenylporphyrinand tetraaza porphyrin the derivative and metalloporphyrin its derivative etc. can be used preferably. The coloring matter used for dye laser can be used for this invention.

[0069] (4) In order to make coloring matter stick to an adsorption semiconductor particulate of coloring matter to a semiconductor particulate a method of immersing a conductive substrate which has the semiconductor particle layer dry well in a solution of coloring matter or applying a solution of coloring matter to a semiconductor particle layer can be used. In the case of the former it is usable in dip coating a dip method the roller method the air knife method etc. In the case of dip coating adsorption of coloring matter may be performed at a room temperature and it may carry out by carrying out heating flowing back as indicated to JP7-249790A. As a latter coating method there are the wire bar method the slide hopper method the extrusion method the curtain method spin method a spray method etc. and printing methods include letterpress offset photogravure screen-stencil etc. A solvent can be suitably chosen according to the solubility of coloring matter. for example alcohols (methanol ethanol and t-butanol.) nitril (acetonitrile and propionitrile.) such as benzyl alcohol nitromethane such as 3-methoxy

propionitrile and halogenated hydrocarbon (dichloromethane.) ether (diethylether.) such as a dichloroethane, chloroform and chlorobenzene dimethyl sulfoxide such as a tetrahydrofuran and amide (N,N-dimethylformamide.) N-methyl pyrrolidone such as NN-dimethyl acetamide 1,3-dimethylimidazolidinone 3-methyl oxazolidinone ester species (ethyl acetate butyl acetate etc.) Carbonic ester ketone (diethyl carbonate ethylene carbonate propylene carbonate etc.) hydrocarbon (acetone 2-butanone cyclohexanone etc.) (hexane petroleum ether benzene toluene etc.) and these mixed solvents are mentioned.

[0070] About viscosity of a solution of coloring matter as well as the time of formation of a semiconductor particle layer various print processes other than the extrusion method are suitable in a viscous liquid (for example 0.01 - 500 Poise) It is possible to use a film with the slide hopper method the wire bar method or suitable spin method and uniform all with hypoviscosity liquid (for example 0.1 or less Poise).

[0071] Thus what is necessary is just to choose an adsorption method of coloring matter suitably according to viscosity of coating liquid of coloring matter coverage a conductive substrate spreading speed etc. When fertilization is considered as short the one of time which coloring matter adsorption after spreading takes as possible is good.

[0072] Since existence of unadsorbed coloring matter becomes the disturbance of element performance it is preferred that washing removes promptly after adsorption. It is preferred that use a wet cleaning tank and an organic solvent like polar solvent such as acetonitrile and an alcohols solvent washes. In order to increase the amount of adsorption of coloring matter heat-treating before adsorption is preferred. After heat-treatment in order to avoid that water sticks to the semiconductor particulate surface it is preferred to make coloring matter adsorb quickly among 40-80 °C without returning to ordinary temperature.

[0073] The amount of all [used] of coloring matter has preferred per [unit surface area (1 m²) / 0.01] - 100 mmol of a conductive substrate. As for the amount of adsorption to a semiconductor particulate of coloring matter it is preferred that they are per [semiconductor particulate 1g / 0.01] - 1 mmol. By considering it as the amount of adsorption of such coloring matter the sensitization effect in a semiconductor is fully acquired. On the other hand if there is too little coloring matter the sensitization effect will become insufficient and if there is too much coloring matter coloring matter which has not adhered to a semiconductor will float and it will become the cause of reducing the sensitization effect.

[0074] Coadsorption of the colorless compound may be carried out to a

semiconductor particulate in order to reduce an interaction of the coloring matter like a meeting. A steroid compound (for example chenodeoxycholic acid) etc. which have a carboxyl group as a hydrophobic compound which carries out coadsorption are mentioned. An ultraviolet ray absorbent can also be used together.

[0075] After adsorbing coloring matter amines may be used and the surface of a semiconductor particulate may be processed in order to promote removal of excessive coloring matter. Pyridine 4-*t*-butylpyridine polyvinyl pyridine etc. are mentioned as desirable amines. When these are fluids it may use as it is and it may dissolve and use for an organic solvent.

[0076] (D) A charge transfer layer charge transfer layer is a layer containing a charge transporting material which has the function to supplement an oxidant of coloring matter with an electron. As an example of a typical charge transporting material which can be used by this invention** As an ion transport material a solution (electrolysis solution) which ion of a redox couple dissolved what is called a gel electrolyte with which gel of a polymer matrix was impregnated in a solution of a redox couple a fused salt electrolyte containing a oxidation reduction counter ion and also a solid electrolyte are mentioned. Carrier movement in ** solid other than a charge transporting material in which ion is concerned can also use an electron transport material and an electron hole (hole) transported material as a material in connection with electrical conduction. These can be used together.

[0077] (1) A fused salt electrolyte fused salt electrolyte is preferred from a viewpoint of coexistence of photoelectric conversion efficiency and endurance. When using a fused salt electrolyte for an optoelectric transducer of this invention For example known iodine salts such as pyridinium salt imidazolium salt a triazolium salt etc. which are indicated to WO 95/No. 18456 JP8-259543 A electrochemistry the 65th volume No. 11923 pages (1997) etc. can be used.

[0078] As fused salt which can be used preferably what is expressed by either a following general formula (Y-a) (Y-b) and (Y-c) is mentioned.

[0079]

[Formula 5]

[0080] Q_{y1} expresses the atom group who can form the aromatic cation of 5 or 6 membered-rings with a nitrogen atom among a general formula (Y-a). As for Q_{y1} it is preferred to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom a hydrogen atom a nitrogen atom an oxygen atom and a sulfur atom.

[0081] A five-membered ring formed of Q_{y1} . An oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring, an isoxazole ring, a thiadiazole ring. It is preferred that they are an oxadiazole ring or a triazole ring. It is more preferred that they are an oxazole ring, a thiazole ring, or an imidazole ring, and it is preferred that they are especially an oxazole ring or an imidazole ring. As for six membered-rings formed of Q_{y1} , it is preferred that they are a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, or a triazine ring, and it is more preferred that it is a pyridine ring.

[0082] A_{y1} expresses a nitrogen atom or a phosphorus atom among a general formula (Y-b).

[0083] A general formula (Y-a) (Y-b) and (Y-c) inner $R_{y1} - R_{y6}$ are alkyl groups (even if it is 1-24 carbon atoms and straight chain shape preferably and is branched state) which is not replaced [substitution or] independently respectively. May be cyclic and For example a methyl group, an ethyl group, a propyl group, an isopropyl group, a pentyl group, a hexyl group, an octyl group, a 2-ethylhexyl group, a 2-octyl group, a decyl group, a dodecyl group, a tetradecyl group, a 2-hexyldecyl group. Alkenyl groups which are not replaced [substitution or] such as an octadecyl group, a cyclohexyl group, and a cyclopentyl group (it may be 2-24 carbon atoms and straight chain shape preferably or may be branched state and) For example a vinyl group, an allyl group, etc. are expressed and it is an alkyl group with 2-18 carbon atoms or an alkenyl group with 2-18 carbon atoms more preferably and is an alkyl group with 2-6 carbon atoms especially preferably.

[0084] Among R_{y1} in a general formula (Y-b) - R_{y4} , a non-aromatic ring in which two or more connect with mutually and they contain A_{y1} may be formed among R_{y1} in a general formula (Y-c) - R_{y6} , two or more may connect mutually and they may form a ring structure.

[0085] A general formula (Y-a) (Y-b) inner Q_{y1} and $R_{y1} - R_{y6}$ may have a substituent and as an example of a desirable substituent, halogen atoms (F, Cl, Br, I, etc.), a cyano group, and an alkoxy group (a methoxy group, an aryloxy group (phenoxy group, etc.), such as an ethoxy group, and an alkylthio group (a methylthio group, etc.), Alkoxy carbonyl groups such as an ethyl thio group (ethoxycarbonyl group, etc.), carbonic ester groups (ethoxycarbonyloxy group, etc.) and an acyl group (an acetyl group, etc.), sulfonyl groups (a methane sulfonyl group, etc.), such as a propionyl group and benzoyl, Acyloxy groups such as a benzenesulfonyl group (an acetoxyl group, a benzoyloxy group, etc.), A sulfonyloxy group (a methane sulfonyloxy group, a toluenesulfonyloxy group, etc.), phosphonyl groups (diethyl phosphonyl group, etc.) and an amide group (an acetylamino group, etc.) Carbamoyl groups (NN-

dimethylcarbamoyl group etc.) such as a benzoylamino group alkyl groups (a methyl group an ethyl group a propyl group an isopropyl group a cyclopropyl group a butyl group a 2-carboxyethyl group benzyl etc.) an aryl group (a phenyl group a tolyl group etc.) Heterocycle groups (a pyridyl group an imidazolyl group a furanyl group etc.) alkenyl groups (a vinyl group 1-propenyl group etc.) etc. are mentioned.

[0086] A compound expressed by a general formula (Y-a) (Y-b) or (Y-c) may form a polymer via Q_{y1} or $R_{y1} - R_{y6}$.

[0087] Such fused salt can also be used together with fused salt which could use it alone or could use it having mixed two or more sorts and which replaced an iodine anion with other anions. As an iodine anion and an anion to replace Halide ion NSC^- (Cl^- Br^- etc.) BF_4^- PF_6^- ClO_4^- $(CF_3SO_2)_2N^-$ $_2N^{(CF_3SO_2)_2}$ $CF_3SO_3^-$ CF_3COO^- Ph_4B^- $_3C^{(CF_3SO_2)}$ etc. are mentioned as a desirable example and it is more preferred that they are $_2N^{(CF_3SO_2)}$ or BF_4^- . Other iodine salts such as LiI can also be added.

[0088] Although an example of fused salt preferably used by this invention is given to below it is not necessarily limited to these.

[0089]

[Formula 6]

[0090]

[Formula 7]

[0091]

[Formula 8]

[0092]

[Formula 9]

[0093]

[Formula 10]

[0094]

[Formula 11]

[0095]

[Formula 12]

[0096] It is more desirable not to use a solvent for the above-mentioned fused salt electrolyte. As for the content of fused salt although the solvent mentioned later may be added it is preferred that it is more than 50 mass % to the whole electrolyte composition. It is preferred that more than 50 mass % is iodine salt among salts and it is still more preferred that it is not less than 70%.

[0097] It is preferred to add iodine to an electrolyte composition as for content of iodine it is preferred that it is [as opposed to / the whole electrolyte composition / in this case] 0.1 to 20 mass % and it is more preferred that it is 0.5 to 5 mass %.

[0098] (2) As for an electrolysis solution when using an electrolysis solution for an electrolysis solution charge transfer layer it is preferred to comprise an electrolyte, a solvent and an additive. An electrolyte of this invention is the combination (as an iodide) of I_2 and an iodide. [LiI and] Metal iodides such as NaIKICsI and CaI_2 or tetra alkyl ammonium iodide Iodine salt of the 4th class ammonium compound such as pyridinium iodide and imidazolium iodide etc. Combination of Br_2 and a bromide (as a bromide) [LiBr and] Metal bromides such as NaBrKBrCsBr and $CaBr_2$ Or others which are the bromine salt of the 4th class ammonium compound such as a tetra alkyl ammonium salt's picture and a pyridinium salt's picture etc. Sulfur compounds such as metal complexes such as a ferrocyanic acid salt-ferricyanic acid salt and ferrocene ferricinium ions sodium polysulfide and alkyl thiol alkyl disulfide viologen coloring matter hydroquinone quinone etc. can be used. An electrolyte which combined iodine salt of the 4th class ammonium compound such as I_2LiI pyridinium iodide imidazolium iodide also in this is preferred in this invention. An electrolyte mentioned above may be mixed and used.

[0099] desirable electrolytic concentration of more than 0.1M is below 15M and more than 0.2M is below 10M still more preferably. Addition concentration of desirable iodine in a case of adding iodine to an electrolyte is less than more than 0.01M 0.5M.

[0100] As for a solvent used for an electrolyte by this invention it is desirable for a dielectric constant to be high in improving ion mobility low and for viscosity to be a compound which improves effective-carriers concentration and can reveal outstanding ion conductivity. As such a solvent carbonate compounds such as ethylene carbonate and propylene carbonate Heterocyclic compounds such as 3-methyl-2-

oxazolidinone dioxane Ether compounds such as diethyl ether ethylene glycol dialkyl ether propylene glycol dialkyl ether polyethylene-glycol dialkyl ether Chain ethers such as polypropylene-glycol dialkyl ether Methanol ethylene glycol monoalkyl ether Propylene glycol monoalkyl ether polyethylene-glycol monoalkyl ether Alcohol such as polypropylene-glycol monoalkyl ether Ethylene glycol propylene glycol polyethylene glycol A polyhydric alcohol class of a polypropylene glycol glycerine etc. acetonitrile Aprotic polar substances such as nitrile compounds such as guru taro dinitrile methoxy acetonitrile propionitrile and benzonitrile dimethyl sulfoxide and sulfolane water etc. can be used.

[0101] At this invention it is J. Am. Ceram. Soc. and 80. (12) Basic compounds such as *tert*-butylpyridine which is indicated to 3157-3171 (1997) 2-picoline 26-lutidine can also be added. in a desirable density range in a case of adding a basic compound more than 0.05M is below 2M. [0102] (3) It can also be used in gel electrolyte this invention making an electrolyte able to gel with techniques such as polymer addition oil gelatinizing agent addition a polymerization containing polyfunctional monomer and crosslinking reaction of polymer (solidification). When making it gel by polymer addition it is "Polymer Electrolyte Reviews-1 and 2" (J. R. MacCallum and C. A. Vincent). [jointly and] Although a compound indicated to ELSEVIER APPLIED SCIENCE can be used especially polyacrylonitrile and polyvinylidene fluoride can be used preferably. By oil gelatinizing agent addition. When making it gel J. Chem. Soc. Japan Ind. Chem. Sec. 46779 (1943) J. Am. Chem. Soc. 1115542 (1989) J. Chem. Soc. Chem. Commun. . 1993390 Angew. Chem. Int. Ed. Engl. 35-1949 (1996) Although Chem. Lett. 1996885 J. Chm. Soc. Chem. Commun. 1997 and a compound indicated to 545 can be used a desirable compound is a compound which has amide structure in molecular structure.

[0103] When making an electrolyte gel by crosslinking reaction of polymer it is desirable to use together polymer and a cross linking agent containing a reactant group which can construct a bridge. A reactant group in which desirable bridge construction is possible In this case nitrogen-containing heterocycle. Are (for example a pyridine ring an imidazole ring a thiazole ring an oxazole ring a triazole ring a morpholine ring a piperidine ring a piperazine ring etc.) and a desirable cross linking agent They are the reagents (for example alkyl halide aralkyl halide sulfonic ester an acid anhydride acid chloride an isocyanate etc.) of two or more organic functions in which an electrophilic reaction is possible to a nitrogen atom.

[0104] (4) In hole transporting material this invention a hole transporting material which combined organicity inorganic matter or these

both instead of an electrolyte can be used.

[0105] (a) As an organic hole transporting material applicable to organic hole transporting material this invention The NN'-diphenyl NN'-bis(4-methoxyphenyl)-(11'-biphenyl)-44'-diamine (J. Hagen et al. Synthetic Metal 89 (1997) 215-220) A 22'77'-tetrakis (NN-di-p-methoxy phenylamine) 99'-spirobifluorene (Nature Vol. 3958 Oct. 1998 p583-585 and WO97/10617) An aromatic diamine compound which connected the 3rd class aromatic amine unit of 11-bis{4-(di-p-tolylamino) phenyl} cyclohexane (JP59-194393A) 44 aromatic amine which two or more fused aromatic rings replaced by a nitrogen atom including two or more tertiary amine represented with **BISU [(N-1-naphthyl) -N-phenylamino] biphenyl (JP5-234681A) Aromatic triamine (U.S. Pat. No. 4923774 JP4-308688A) NN'-diphenyl N which have starburst structure with a derivative of triphenylbenzene. Aromatic diamines such as N'-bis(3-methylphenyl)-(11'-biphenyl)-44'-diamine (U.S. Pat. No. 4764625) alpha-alpha-alpha'-alpha'-tetramethyl alpha and alpha'-bis(4-di-p-tolylamino phenyl)-p-xylene (JP3-269084A) As a p-phenylene diamine derivative and the whole molecule a triphenylamine derivative unsymmetrical in three dimensions (JP4-129271A) A compound which an aromatic diamino group replaced by a pyrenyl group (JP4-175395A) Aromatic diamine which connected the 3rd class aromatic amine unit by ethylene (JP4-264189A) Aromatic diamine which has styryl structure (JP4-290851A) A benzylphenyl compound (JP4-364153A) a thing which connected tertiary amine by a fluorene group (JP5-25473A) Triamine compound (JP5-239455A) pith dipyridyl aminobiphenyl (JP5-320634A) NN and N-triphenylamine derivative (JP6-1972A) Aromatic amine shown in aromatic diamine (JP7-138562A) which has FENO affected group in structure a diaminophenyl phenanthridine derivative (JP7-252474A) etc. can be used preferably.

[0106] An alpha-octylthiophene and alpha and omega-dihexyl- alpha-octylthiophene (Adv. Mater. 1997 9 No. 7 p557) A hexadodecyl DODESHI thiophene (Angew. Chem. Int. Ed. Engl. 1995 34 No. 3 and p303-307) Oligo thiophene compounds such as 28-dihexyl ANSURA [23-b:67-b'] dithio Foehn (JACS Vol. 120 No. 4-1998 p664-672) Polypyrrole (K. Murakoshi et al.; Chem. Lett. 1997 p471) Handbook of Organic Conductive Molecules and Polymers Vol. 1, 2, 3, 4 (NALWA work.) Polyacetylene indicated to WILEY publication and its derivative Poly (p-phenylene) and its derivative poly (p-phenylene vinylene) and its derivative poly thienylene vinylene and its derivative a polythiophene and its derivative poly aniline and its derivative Conductive polymers such as a polytoluidine and its derivative can be used preferably.

[0107] In order to control a dopant level to an electron hole (hole)

transported material as indicated to Nature Vol. 395 8 Oct. 1998 and p583-585. In order to add a compound containing a cation radical like tris (4-bromophenyl) aminium hexachloro antimonate or to perform potential control on the surface of an oxide semiconductor (compensation of a space charge layer) a salt like Li [(CF₃SO₂)₂N] may be added.

[0108] (b) A p type inorganic compound semiconductor can be used as an inorganic hole transporting material inorganic matter hole transporting material. As for a p type inorganic compound semiconductor of this purpose it is preferred that a band gap is not less than 2 eV and it is preferred that it is not less than 2.5 eV. Ionization potential of a p type inorganic compound semiconductor needs to be smaller than ionization potential of conditions to a coloring matter adsorption electrode which can return an electron hole of coloring matter. Although the desirable range of ionization potential of a p type inorganic compound semiconductor changes with coloring matter to be used generally it is preferred that it is [not less than 4.5 eV] 5.5 eV or less and it is preferred that it is [not less than 4.7 eV] 5.3 eV or less. A desirable p type inorganic compound semiconductor is a compound semiconductor containing copper of monovalence. As an example of a compound semiconductor containing copper of monovalence. ** CuI CuSCN CuInSe₂ Cu(InGa) Se₂ CuGaSe₂ Cu₂O CuSCuGaS₂ CuInS₂ CuAlSe₂ etc. are mentioned. Also in this CuI and CuSCN are preferred and CuI is the most preferred. As other p type inorganic compound semiconductors GaPNiOCoFeOBi₂O₃MoO₂Cr₂O₃ etc. can be used.

[0109] As for desirable Hall mobility of a charge transfer layer containing a p type inorganic compound semiconductor more than 10⁻⁴ cm²/V-sec is below 10⁻⁴ cm²/V-sec More than 10⁻³ cm²/V-sec is below 10⁻³ cm²/V-sec still more preferably. Desirable conductivity of a charge transfer layer of more than 10⁻⁸ S/cm is below 10⁻² S/cm and more than 10⁻⁶ S/cm is 10 or less S/cm still more preferably.

[0110] (5) Two kinds of methods can be considered about a formation method of a formation charge transfer layer of a charge transfer layer. One pastes a counter electrode together previously on a semiconductor particulate contained layer which made sensitizing dye support and it is the method of putting a liquefied charge transfer layer between the gap. Another is the method of giving a charge transfer layer directly on a semiconductor particulate contained layer and a counter electrode will be given after that.

[0111] A vacuum process which uses a pressure lower than an ordinary pressure process and ordinary pressure which use capillarity by immersion etc. as how to put a charge transfer layer in the case of the

former and replaces the gaseous phase by the liquid phase can be used. [0112] In the case of the latter in a wet charge transfer layer a counter electrode will be given with un-drying and a liquid leakage control measure of an edge part will also be taken. There is also a method of applying by a wet type in the case of a gel electrolyte and solidifying by methods such as a polymerization and a counter electrode can also be given after drying and fixing in that case. As a method of giving a wet organic hole transporting material besides an electrolysis solution and a gel electrolyte dip coating the roller method a dip method the air knife method the extrusion method the slide hopper method the WAYABA method spin method a spray method the cast method various print processes etc. can be considered like grant of a semiconductor particulate contained layer or coloring matter.

[0113] In the case of an electron hole (hole) transported material of a solid electrolyte or a solid charge transfer layer can be formed by dry membrane formation processing of a vacuum deposition method a CVD method etc. and a counter electrode can also be given after that. An organic hole transporting material can be introduced into an inside of an electrode with techniques such as a vacuum deposition method the cast method the applying method a spin coat method dip coating an electrolytic polymerization method and photoelectrical depolymerization method. Also in an inorganic solid compound it can introduce into an inside of an electrode with techniques such as the cast method the applying method a spin coat method dip coating and an electrolytic plating method.

[0114] When considering fertilization although correspondence is also possible by closing an edge part promptly after painting in the case of an electrolysis solution which cannot be solidified or a wet hole transporting material In the case of a hole transporting material which can be solidified after carrying out film formation of the electron hole transporting bed by wet grant it is more preferred to solidify by methods such as photopolymerization and a heat radical polymerization. Thus what is necessary is just to choose a film grant method suitably according to liquid nature or a process condition.

[0115] As moisture in a charge transfer layer 10000 ppm or less are 2000 ppm or less desirable still more preferably and is 100 ppm or less especially preferably.

[0116] (E) The counter electrode counter electrode needs to act as an anode of an optoelectric transducer and the same transparent conductive material as the above-mentioned conductive substrate needs to be used for it from the necessity for light transmission except a counter electrode of the bottom of the heap. As a conducting material used for a

counter electrode conductive layer metal carbon (for example platinum gold silver copper aluminum magnesium rhodium indium etc.) or conductive metallic oxide (what doped fluoride to an indium tin multiple oxide and tin oxide) is mentioned. Also in this platinum gold silver copper aluminum and magnesium can be preferably used as a counter electrode layer. An example of a desirable supporting board of a counter electrode is glass or a plastic is applied or vapor-deposited and uses the above-mentioned conducting agent for this. Although thickness in particular of a counter electrode conductive layer is not restricted 3 nm - 10 micrometers are preferred. When a counter electrode conductive layer is metal the thickness is 5 micrometers or less preferably and ranges of it are 5 nm - 3 micrometers still more preferably. Surface resistance of a counter electrode layer is so good that it is low. As a range of desirable surface resistance it is below 80 ohms / ** and is below 20 ohms / ** still more preferably.

[0117] The counter electrode should just stick the conductive layer side of a substrate which applies plates or vapor-deposits a conducting material directly on a charge transfer layer (PVDCVD) or has a conductive layer. As well as a case of a conductive substrate when especially a counter electrode is transparent it is preferred to use a metal lead in order to lower resistance of a counter electrode. A fall of incident light quantity by desirable construction material of a metal lead and an installation method and metal lead installation is the same as a case of a conductive substrate.

[0118] A counter electrode of the bottom of the heap may be opaque (when there is no photosensitive layer in an opposite hand of a under from a counter electrode i.e. a light incidence face). From a viewpoint of raising a capturing rate of light a counter electrode of the bottom of the heap is so preferred that light reflex nature is large. Layer structure of a counter electrode conductive layer which consists of conductive materials may be sufficient as a counter electrode of the bottom of the heap and it may comprise a counter electrode conductive layer and a supporting board.

[0119] (F) When using an electron transport material and a hole transporting material for other layer charge transfer layers in order to prevent a short circuit of a counter electrode and a conductive substrate it is preferred to paint a thin film layer of a conductive substrate and a semiconductor precise between photosensitive layers as an under coat beforehand. TiO_2 , SnO_2 , Fe_2O_3 , WO_3 , ZnO and Nb_2O_5 are preferred as an under coat and it is TiO_2 still more preferably. An under coat can be painted by Electrochimi. Acta 40 and the spray pyrolysis method

indicated to 643-652 (1995). Desirable thickness of an under coat is 5-1000 nm or less and its 10-500 nm is still more preferred.

[0120] Functional layers such as a protective layer and an antireflection layer may be provided in both a conductive substrate and both [one side or] which act as an electrode. When forming such a functional layer in a multilayer, the simultaneous multilayer applying method and the serial applying method can be used but from a viewpoint of productivity, the simultaneous multilayer applying method is preferred. In the simultaneous multilayer applying method, when productivity and the homogeneity of a coat are considered, the slide hopper method and the extrusion method are suitable. Vacuum deposition, the sticking method, etc. can be used for formation of these functional layers according to the construction material.

[0121]

[Example] Hereafter, an example explains this invention concretely. At this example, the laminate type battery which consists of lamination of drawing 4 and an equivalent circuit of drawing 7 was assembled in the following procedure.

[0122] 1. On one side of the substrate of alkali free glass with a base material thickness for photosensitive layers of 0.4 mm of the production 1, the topmost part of a transparent conductive base material. The whole surface was uniformly coated with fluoride dope type diacid-ized tin with the CVD method and surface resistance about 15 ohm/[600 nm in thickness and] **and light transmittance (500 nm) formed the transparent conductive base material which covered 85% of conductive diacid-ized tin membrane on one side.

2) On one side of the substrate of alkali free glass with a lowermost base material thickness [in parts intermedia] for photosensitive layers of 0.4 mm. The whole surface is uniformly coated with fluoride dope type diacid-ized tin with a CVD method like above. On one side, surface resistance about 6 ohm/[200 nm in thickness and] **and light transmittance (500 nm) covered 90% of conductive ITO (indium tin oxide) with the CVD method and both sides have further already formed the base material covered with the transparent conducting film. An ITO film is used as a counter electrode as a ground in which diacid-ized tin membrane supports the photosensitive layer of a dye sensitizing semiconductor in these conducting films.

[0123] 2. In accordance with the manufacturing method of a statement in the J. Am. Ceramic Soc. 80 volume of preparation C. J. Barbe and others of titanium dioxide particle content coating liquid and the paper of p3157, Titanium tetra isopropoxide was used for the titanium material, the

temperature of the polymerization reaction in the inside of autoclave was set as 230 °C and the titanium dioxide dispersed matter of 11 % of the weight of titanium dioxide concentration was compounded. The average size of the primary particle of the obtained titanium dioxide particles was about 10 nm.

[0124] 30% of the weight of the polyethylene glycol (the average molecular weight 20000 the Wako Pure Chem make) was added and kneaded to the titanium dioxide to this dispersed matter and the viscous emulsion for spreading was obtained.

[0125] 3. This coating liquid is applied to the diacid-ized tin covering surface side of two sorts of transparent conductive substrates produced by 1 and 2 of the production above 1 of a titanium dioxide semiconductor particle layer by a thickness of 100 micrometers with a doctor blade method. After drying for 60 minutes at 25 °C it calcinated for 30 minutes at 500 °C with the electric furnace and the titanium dioxide layer was covered. The coating volume of the titanium dioxide was 10 g/m² and thickness was 8 micrometers.

[0126] 4. As sensitizing dye to 400-600 nm of preparation of a coloring matter adsorption solution which has absorption in the visible wavelength region of short wavelength comparatively. The poly methine coloring matter (coloring matter A) of the following structural formula was dissolved in the mixed solvent of ethanol:DMSO (95:5) by the concentration of 0.0001 mol / L. 0.04 mol/L addition of the chenodexycolic acid was carried out as an additive agent and the solution A for adsorption of the sensitizing dye used for the topmost photosensitive layer was prepared.

[0127]

[Formula 13]

[0128] As sensitizing dye which has absorption in the long wavelength side to 750 nm and has an absorption peak in blue - green regions. It dissolved in the mixed solvent of the acetonitrile:t-butanol (1:1) which dried Ru complex pigment (coloring matter R-1) of the above-mentioned example at concentration 3×10^{-4} mol/L and the adsorption solution B of the sensitizing dye used for the photosensitive layer of pars intermedia was prepared.

[0129] As red sensitizing dye which has absorption to 900 nm in the long wavelength side. Dissolve in the mixed solvent of acetonitrile:t-butanol (1:1) at concentration 5×10^{-4} mol/L and further Ru complex pigment (coloring matter R-10) of an example as a meeting inhibitor-

nonylphenoxyethoxy BUCHIRUSURUHON acid sodium was added 0.5% of the weight it dissolved and the solution C for adsorption of the sensitizing dye used for the lowermost photosensitive layer was prepared.

[0130]5. Among the substrates with which the adsorption titanium dioxide particulate layer of coloring matter was painted both sides immersed the conductive substrate in the above-mentioned coloring matter solution A for adsorption to each at the coloring matter solutions B and C for adsorption and one side neglected the conductive substrate (for topmost part photosensitive layers) at 40 °C under stirring for 3 hours.

Thus after making a titanium dioxide particulate layer dye coloring matter the electrode was washed by acetonitrile and the dye sensitizing electrode used for the object for the topmost part the object for parts intermedia and three sorts of photosensitive layers for the bottoms was produced.

[0131]6. It was failed to scratch the surrounding layer and the euphotic zone of area 2 of 1.0 cm was fabricated so that it might become one-side the square of 10 mm about the TiO_2 layer of the dye sensitizing TiO_2 electrode of three sorts of production of a photoelectric cell. These substrates were piled up in order of the topmost part-parts intermedia-bottom so that a photosensitive layer and a counter electrode layer might face each other according to the lamination of drawing 4. Under the lowermost photosensitive layer the platinum vacuum evaporation glass substrate was arranged as a counter electrode of light reflex nature. Among these substrates as a frame-shaped spacer it inserted and the polyethylene film (20 micrometers in thickness) of thermo-compression-bonding nature was piled up so that a photosensitive layer might be surrounded and two or more substrates which heated the spacer part at 120 °C and were laminated were stuck by pressure and it fixed. Furthermore the seal of the edge part of a cell was carried out with epoxy resin adhesive.

[0132]Next it let the stoma for electrolysis solution pouring in beforehand provided in the corner part of the spacer pass and the room temperature fused salt which comprises the presentation of Y7-2/Y8-1 / iodine = 15:35:1 (weight ratio) as an electrolysis solution was infiltrated into inter-electrode space by a 50 °C basis using capillarity. All of the above cell fabrication process and the process of electrolysis solution pouring were carried out in above-mentioned dew point -60 °C dry air. After pouring of fused salt the cell was attracted under the vacuum for several hours the inside of a cell was deaerated and low melting glass stopped the stoma for pouring in after the end.

[0133]Thus the dye sensitizing semiconductor wet type photocell (example

1) of this invention in which the photosensitive layer from which a wavelength characteristic differs was laminated was produced.

[0134]The lamination type cell (examples 5 and 6) which changed and laminated an order of lamination of a photosensitive layer that three sorts of sensitization wavelength areas differed in the similar way was also produced (herein learned from the above-mentioned method and the substrate of one side conductivity was suitably used for coloring matter adsorption of the topmost photosensitive layer). Only two of three sorts of photosensitive layers were laminated and the lamination type cell (examples 2-4 and 7) which has arranged the light reflex nature platinum counter electrode to the bottom of the heap was also produced.

[0135]In the long wavelength photosensitive layer it replaced with the titanium oxide layer which carried out sensitization with the R-10 above-mentioned coloring matter and the lamination type cell (example 8) using the long wavelength photosensitive layer which made the same coloring matter R-10 stick to a porous diacid-ized tin semiconductor layer was also produced. The photosensitive layer of this diacid-ized tin semiconductor has the character [open circuit voltage / (Voc)] fundamentally in which it is low compared with the above-mentioned titanium oxide semiconductor photosensitive layer.

[0136]The lamination type cell (comparative examples 1-4) which laminated the same nature photosensitive layer of a dye sensitizing semiconductor as an object for comparison and the single cell (comparative examples 5-8) which consists of a single photosensitive layer were prepared for others.

[0137]7. The xenon lamp (USHIO electrical and electric equipment) of the measurement 500W of photoelectric conversion efficiency was equipped with the compensation filter for sunlight simulations (AM1.5 direct by Oriel) and the incident light intensity to the cell irradiated with the imitation sunlight adjusted to $100\text{mW}/\text{cm}^2$.

[0138]The electric generating power of the produced photoelectrochemical cell was inputted into the current potential measuring device (sauce major unit 238 type made from a case rhe) and current/voltage characteristics were measured. Child (%) and the efficiency IPCE for incident light quantity of photoelectric current generating measured in the short circuit current density (Jsc) of the photoelectrochemical cell called for by this and 650 nm of red spectrum region the open circuit electromotive voltage (Voc) and the energy conversion efficiency (η) were indicated to Table 1 with the lamination of the lamination cell.

[0139]

[Table 1]

[0140]The following things are clear from the result of Table 1.

1) The comparative examples 1-4 which laminated the same photosensitive layer of the optical absorption wavelength range comparing with the single cell (comparative examples 5-8) used as the component -- the short circuit current density J_{sc} and an energy conversion efficiency -- most -- J_{sc} and the energy conversion efficiency of Examples 1-8 of the laminated structure according to the conditions of this invention improve to change not being seen.

[0141]2) From comparison of Example 3 and Example 4 when the upper levels' photosensitive layer is the same give a high energy conversion efficiency with as high J_{sc} as that by which the absorption wavelength of the photosensitive layer put on a bottom-of-the-heap part attains to long wavelength more.

[0142]3) Give a high energy conversion efficiency in the lamination cell using the combination of the same single cell from comparison of Examples 1 and 6 with J_{sc} with higher the long wavelength end of the optical absorption wavelength range arranging in the upper levels (incidence side) in order of short wavelength more.

[0143]4) Although V_{oc} is falling in a lamination cell from comparison of Examples 1 and 8 in Example 8 from which V_{oc} of a single cell differs in the range which are 0.42-0.66V compared with Example 1 which has the open circuit electromotive voltage V_{oc} of the single cell which constitutes a cell in 0.65-0.66V and the almost near range. It is because this has a rate as large as 19% which the standard deviation of V_{oc} of three sorts of single cells gives to average value and change of V_{oc} between single cells is large. However Example 8 has the merit that J_{sc} is high as compared with the comparative examples 1-8.

[0144]Thus it turns out that the lamination type solar cell made in accordance with the method of this invention is excellent in respect of condensing efficiency and J_{sc} and IPCE reflecting it and gives a high energy conversion efficiency from the result of the above-mentioned example. It turns out that a higher energy conversion efficiency is given in the cell which satisfies the various requirements especially shown in the claim.

[0145]

[Effect of the Invention]As explained in full detail above the photoelectric transducer of this invention excels [condensing efficiency] in the energy conversion efficiency highly. Therefore the photoelectric cell which consists of this photoelectric transducer is

very effective as a solar cell.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 2] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 3] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 4] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 5] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 6] It is a fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.

[Drawing 7] It is a sectional view showing the equivalent circuit of the desirable optoelectric transducer of this invention.

[Drawing 8] It is a sectional view showing the equivalent circuit of the desirable optoelectric transducer of this invention.

[Description of Notations]

1 ... Optoelectric transducer

1a ... Leak hole

10 ... Conductive layer

10a ... Transparent conductive layer

11 ... Metal lead

20 20a 20b 20c ... Photosensitive layer

21 ... Semiconductor particulate

22 ... Coloring matter

23 ... Charge transporting material

30 ... Charge transfer layer

40 ... Counter electrode conductive layer

40a ... Transparent counter electrode conductive layer

50 ... Substrate

50a ... Transparent substrate

60 ... Under coat

2 ... External circuit
